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Trifluoroethoxyphosphazenes have been converted by metalled olefinic phosphazenes and these yield stable derivatives when treated with alectrophiles.

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PHOSPHAZENES WITH OLEFINIC SIDE GROUPS: PROTON ABSTRACTION REACTIONS OF FLUOROALKOXY DERIVATIVES

by

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Prepared for publication in Organometallics

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Phosphazenes with Olefinic Side Groups: Proton Abstraction Reactions of Fluoroalkoxy-Derivatives

Harry R. Allcock*, Paul R. Suszko, and Thomas L. Evans

Contribution from The Department of Chemistry, The Pennsylvania State
University, University Park, Pennsylvania 16802

ABSTRACT: The cyclic phosphazenes, $N_3P_3(OPh)_5OCH_2CF_3$, $[NP(OPh)(OCH_2CF_3)]_3$ and $[NP(OCH_2CF_3)_2]_3$ undergo dehydrofluorination and deprotonation when treated with n-butyllithium at −78°C to form metallated intermediates of formula $N_3P_3(OPh)_5OC(Li){=}CF_2$, $[NP(OPh)(OC(Li){=}CF_2)]_3$ and $[NP(OC(Li){=}CF_2)_2]_3$, respectively. These species are stable in solution at −78°C, but react with electrophiles such as 2-propanol, 2-propan(ol-d), methyl iodide, or triphenyltin chloride to yield the cyclophosphazenes with $-OC(H){=}CF_2$, $-OC(D){=}CF_2$, $-OC(CH_3){=}CF_2$, or $-OC(SnPh_3){=}CF_2$ side groups. The reactions were monitored by the use of ^{19}F NMR spectroscopy. A reaction mechanism is proposed. Comparisons are made with the reactions between n-butyllithium and trifluoroethoxy-substituted cyclic tetrameric and high polymeric phosphazenes.

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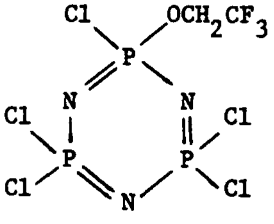
The synthesis and properties of many fluoroalkoxy phosphazene compounds have been described in recent years.[1-6] The simplest species of this type (such as 1, 2, or 3) can be obtained by the reaction of sodium trifluoroethoxide with hexachlorocyclotriphosphazene, $(NPCl_2)_3$.[4] Moreover, high polymeric analogues are accessible via the interaction of sodium trifluoroethoxide with poly(dichlorophosphazene), $(NPCl_2)_n$.[7,8] High polymers can also be prepared by the copolymerization of fluoroalkoxycyclotriphosphazenes with $(NPCl_2)_3$.[4]

The ease of preparation of fluoroalkoxy-substituted phosphazenes prompted us to explore the possibility that such compounds might themselves be substrates for further structural modification via reactions of the fluoroalkoxy side groups. The objective was to develop a new technique for the synthesis of hitherto inaccessible cyclic and high polymeric phosphazenes, especially those that contain olefinic and metallo side groups.

The reactions examined here make use of the interaction between an organometallic reagent and an $-OCH_2CF_3$ side group to generate an $-OC(M){=}CF_2$ unit. Subsequent treatment with an electrophile was designed to yield an $-OC(R){=}CF_2$ side group. Metallic units could be introduced as components of the group, R.

Results and Discussion

Synthesis of Fluoroalkoxy Derivatives. The fluoroalkoxy-phosphazene precursors used in this study were prepared in the following way. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was allowed to react with sodium trifluoroethoxide to yield products with various degrees of substitution that depended on the mole ratio of the reactants.[4] Thus, mono-(trifluoroethoxy)-pentachlorocyclotriphosphazene, 1, trans-non-gem-tris-(trifluoroethoxy)-trichlorocyclotriphosphazene, 2, and hexakis-(trifluoroethoxy)-cyclotriphosphazene, 3, were obtained directly. For the purposes of this study, compounds 1 and 2 were each treated with an excess of sodium phenoxide in order to replace the remaining chlorine atoms with phenoxy groups, yielding 4 and 5, respectively. The phenoxy groups were introduced to reduce the possibility of subsequent side reactions that might be expected with 1 and 2.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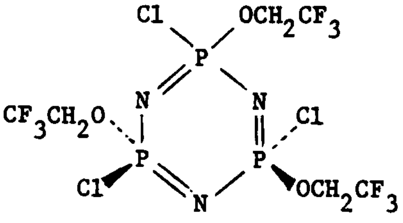
P
N
N
Cl
Cl
Cl
Cl
P
P
N

1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N
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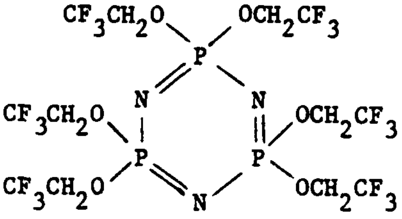
Cl
Cl
P
P
OCH$_2$CF$_3$
N

2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P
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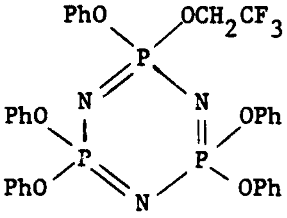
OCH$_2$CF$_3$
P
P
N

3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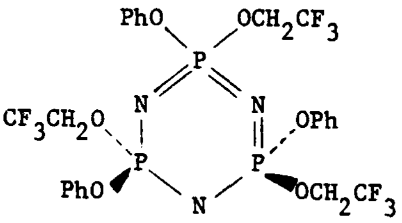
P
N
N
PhO
OPh
PhO
OPh
P
P
N

4


PhO
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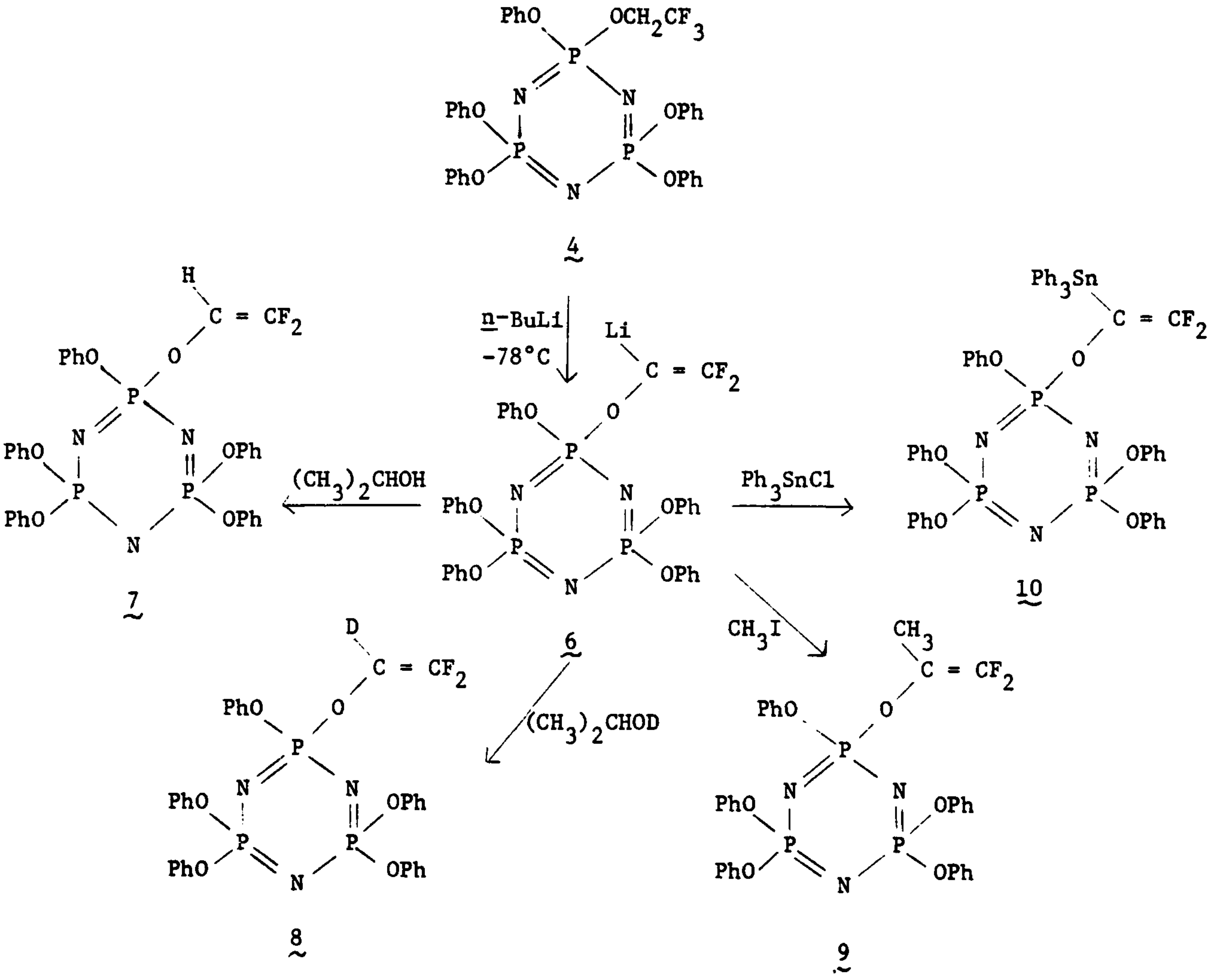
P
N
N
CF$_3$CH$_2$O
OPh
PhO
OCH$_2$CF$_3$
P
P
N

5

The structures of compounds 1, 2, and 3 were confirmed by comparisons of the ^{31}P NMR spectral data with published values.[4] The ^{31}P NMR spectrum of the new species, 4, consisted of a second order AB$_2$ pattern with $\delta_A = 13.5$ ppm and $\delta_B = 9.8$ ppm ($J_{AB} = 87.5$ Hz).[9] Compound 5 showed an AB$_2$ spectrum with $\delta_A = 13.3$ ppm and $\delta_B = 12.9$ ppm (the spectrum was a near-limiting AB$_2$ system:

thus, J_{AB} was not determined). The ^{19}F NMR spectra[10] of 1, 3, and 4 similarly revealed a triplet at ∼38 ppm downfield from fluorobenzene (Table I). The ^{19}F NMR resonances for the fluorine atoms in 2 and 5 appeared as multiplets due to the slight differences in chemical shift between the cis and trans trifluoroethoxy groups.

General Reaction Pathway. The metallation and subsequent substitution sequence for 4 is outlined in Scheme 1. Similar transformations were also carried out with species 5 and 3, as discussed in a later section.



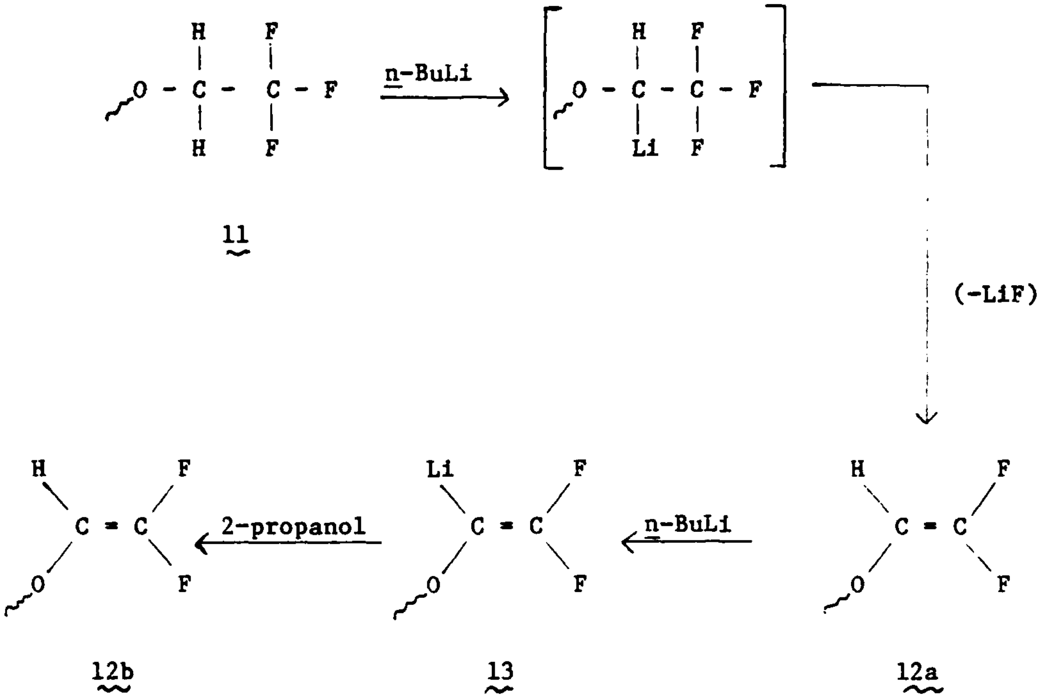
Scheme 1

Specifically, 4 reacted with two molar equivalents of *n*-butyllithium (in THF at -78°C), via total deprotonation of the trifluoroethoxy group, to form the lithiated vinyl ether, 6. This carbanion was then allowed to react with 2-propanol, 2-propan(ol-d), methyl iodide, or triphenyltin chloride to yield the substituted olefinic products, 7, 8, 9, or 10. In principle, a wide variety of electrophilic reagents could be used in this reaction. The lithiated olefin was stable at -78°C, but reacted readily following addition of an electrophile. The resultant olefin-substituted phosphazenes (7-10) represent a new series of derivatives that cannot be prepared by alternative routes.

Phosphazene compounds of this type are of interest for several reasons. First, they represent potential "monomers" that could be incorporated into organic polymers via copolymerization through the vinyl group. Second, the cyclic phosphazenes which contain more than one olefinic side group could function as crosslinking agents for organic or inorganic polymers that contain the appropriate side groups. Third, the fluoro-olefin function is a potential ligand for the incorporation of transition metal complexes.

Reaction Mechanism. The proton abstraction process at different temperatures was monitored by ^{19}F NMR spectroscopy. ^{19}F NMR spectroscopy was an exceptionally useful technique for following the course of this reaction, whereas ^{31}P NMR spectroscopy provided little useable information.[11] The sequence of ^{19}F NMR spectral changes was compatible with the generalized mechanism shown in Scheme 2.

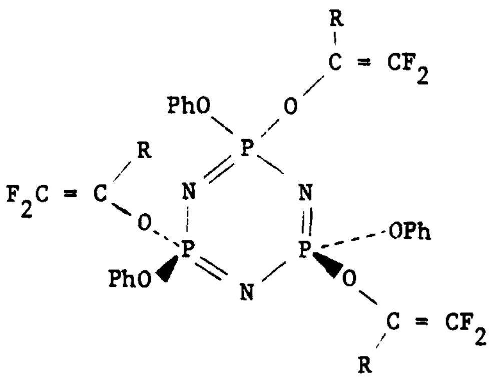
Thus, *n*-butyllithium abstracts a proton from 11 to form a transient carbanion, which eliminates a fluoride ion to form 12a. The dehydrofluorinated product, 12a, is then deprotonated rapidly by additional *n*-butyllithium to give 13, which remains stable at -78°C until quenched. The metallated vinylic side group, 13, can also be generated by treatment of the independently isolated product, 12b, with *n*-butyllithium at -78°C.



Scheme 2

The specific experimental evidence for the conversion of 4 to 7 was as follows. The ^{19}F NMR spectrum of 4 consisted of a triplet centered at 37.8 ppm (Fig. 1a). Addition of less than 0.2 equiv of *n*-butyllithium (at -78°C) resulted in the appearance of two new resonances: (1) a doublet of doublets centered at 16.4 ppm, and (2) a doublet centered at -3.6 ppm. These resonances correspond to the olefinic compound 7.[12] On further addition of *n*-butyllithium, these peaks disappeared and were replaced by a doublet centered at 23.7 ppm and a doublet centered at -13.2 ppm (Fig. 1b). These resonances correspond to the non-equivalent fluorine atoms in 6. As more *n*-butyllithium was added, these peaks continued to grow at the expense of the triplet at 37.8 ppm from the starting material. A quantitative conversion of 4 to 6 had taken place (Fig. 1c) after two molar equivalents had reacted. The olefinic compound, 7, possesses a more acidic proton than the starting material, 4, and is, therefore, preferentially deprotonated during the addition of successive aliquots of *n*-butyllithium. Addition of 2-propanol to 6 at -78°C resulted in the disappearance of 6 and the formation of 7, which showed ^{19}F NMR spectra identical to the one generated earlier (Fig. 1d and e). When 6 was allowed to warm slowly to room temperature, the associated ^{19}F NMR spectrum disappeared. Compound 6 decomposed rapidly above -20°C, most likely with loss of volatile fluorocarbon byproducts. The reactions of 6 with the various reagents were virtually instantaneous at -78°C. This is true even for reactions with the bulky electrophile, Ph_3SnCl.

Olefinic Derivatives of 5. The techniques described in the foregoing sections were also applied to compound 5, with similar results. Six molar equivalents of *n*-butyllithium were required to fully deprotonate 5 to form the intermediate tri-lithio carbanion, 14. This species reacted readily with the electrophiles mentioned previously to yield the substituted cyclotriphosphazenes, 15, 16, 17, and 18.



R =	
-Li	14
-H	15
-D	16
$-CH_3$	17
$-SnPh_3$	18

The ^{19}F NMR spectra associated with the formation of the methyl substituted tri-olefinic product, 17, are shown in Figure 2. The ^{19}F NMR spectrum of 5 is not a clean triplet (by contrast with the spectrum of 4). Rather, it has a quartet-type multiplicity. This slight difference in chemical shift between the cis and trans fluoroalkoxy groups is more clearly manifest in the ^{19}F NMR spectra associated with 14 and 17 (Fig. 2b and c). The superimposed ^{19}F NMR resonances from the cis and trans fluoroalkenoxy groups in these compounds have sufficiently different chemical shifts to result in a distinct separation. Presumably, the doublet of lesser intensity in each fluorine resonance corresponds to the trans group.

Metallation and Substitution of 3. All six trifluoroethoxy groups in 3 could also be converted to lithiated vinylic ether groups by reaction with an excess of *n*-butyllithium. Although, in principle, twelve molar equivalents should be required to effect complete deprotonation, in practice, an excess of *n*-butyllithium is required to drive the equilibrium toward formation of the product. The hexa-lithio carbanionic intermediate, 19, showed an ^{19}F NMR spectrum that consisted of two broadened multiplets centered at roughly the same positions as observed for each fluorine in 6. The complex resonances are a result of the non-equivalence of the fluorine atoms caused by proximal charge repulsions in the hexa-lithio species. Quenching of this intermediate with 2-propanol, 2-propan(ol-d), or methyl iodide yielded 20, 21, or 22, which gave ^{19}F NMR spectra similar to those of 7, 8, or 9, respectively.

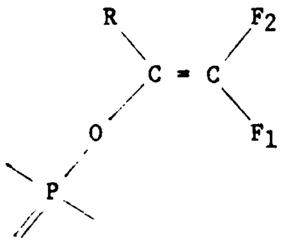
Although ^{19}F NMR resonances were detected for $-OC(SnPh_3)=CF_2$ groups when 19 was treated with Ph_3SnCl, a hexa-substituted derivative was not isolated, probably because of the unfavorable steric interactions that would exist in the product. The yields of the olefinic products were lower for the hexa-substituted compounds than for the mono- or tri-substituted derivatives following considerable decomposition during the isolation steps. Thus, the hexa-olefinic compounds were not as stable as the mono- or tri-olefinic derivatives. In the latter species, the phenoxy groups presumably serve as stabilizing components by providing a steric shield around the molecule.

Species 20-22 appeared to undergo hydrolysis when exposed to atmospheric moisture for prolonged periods of time. Mass spectral analysis of the decomposition products indicated the presence of lower molecular weight species in addition to products that could arise from the addition of water across the carbon-carbon double bond.

$[N{=}P(OC(R){=}CF_2)]_3$

R		
R =	-Li	19
	-H	20
	-D	21
	$-CH_3$	22

Characterization of Products. The phosphazene compounds described in the foregoing sections were colorless oils, with the exception of 3 and 5, which were white crystalline materials (m.p. = 49°C and 55°C, respectively). The identity of each compound was confirmed by a combination of NMR spectroscopy, infrared spectroscopy, and mass spectrometry. The ^{19}F NMR spectroscopic data are listed in Table I. "Cis" and "trans" fluorine atoms are distinguished by the numbering system shown below.



In general, *trans* coupling constants are larger than the corresponding *cis* coupling constants in fluoro-olefinic compounds. This is reflected, for example, in the ^{19}F NMR spectrum of 7. Here, the value of J_{F_1H} was 15 Hz, whereas J_{F_2H} was of the same order as J_{F_2P} (ca. 6 Hz) and was not well resolved (Fig. 1e). J_{F_2P} was resolved in the spectrum of 8, where hydrogen was replaced by deuterium, and has a value of 6 Hz (Fig. 3a). The F_1 atom in 8 shows no observable *cis* coupling to the ring phosphorus atom. The ^{19}F NMR spectra of 8, 9, and 10 are shown in Figure 3.

The ^{31}P NMR spectra of the compounds 4, 7, 8, 9, and 10 were all complex second order AB_2 spin systems appearing in the range 8 to 14 ppm.[9] The corresponding compounds 5, 15-18, and 3, 20-22 showed singlets in the ^{31}P NMR spectra in the range, 11 to 17 ppm.

Representative ^{13}C NMR spectra were obtained for the products 2 and 15. For compound 2, the following data were collected:[13] $-PO\underline{C}H_2CF_3$: $\delta = 63.7$, $J_{CF} = 39$, $J_{CH} = 152$, $J_{CP} = 5$; $-POCH_2\underline{C}F_3$: $\delta = 122.0$, $J_{CF} = 278$, $J_{CH} = 8$, $J_{CP} = 13$. For compound 15, the data were as follows:[14] $-PO\underline{C}H{=}CF_2$: $\delta = 100.3$, $J_{CF} = 14$, $J_{CF} = 60$, $J_{CH} = 200$; $-POCH{=}\underline{C}F_2$: $\delta = 156.3$, $J_{CF} = 283$; $-PO\underline{Ph}$: $\underline{C}_{ipso}$ $\delta = 149.7$; $\underline{C}_{ortho}$ $\delta = 120.5$, $J_{CH} = 163$; $\underline{C}_{meta}$ $\delta = 129.4$, $J_{CH} = 162$; $\underline{C}_{para}$ $\delta = 125.2$, $J_{CH} = 162$. The proton-decoupled and proton-undecoupled ^{13}C NMR spectra of 15 are shown in Fig. 4.

All the fluoro-olefinic compounds showed prominent absorptions in the region, 1600-1800 cm^{-1} ($-C{=}CF_2$ vibration) and 1100-1300 cm^{-1} ($-P{=}N-$ vibrations).

Comparisons with Cyclic Tetrameric and High Polymeric Phosphazenes. The trifluoroethoxy groups in $[NP(OCH_2CF_3)_2]_4$ (23) or $[NP(OCH_2CF_3)_2]_n$ (24) did not react with *n*-butyllithium in the straightforward manner found for the cyclic trimer. Instead, complex mixtures of products were formed that showed broad, diffuse ^{31}P or ^{19}F NMR peaks. No resonances corresponding to olefinic-type atoms were detected.

A number of alternative reaction pathways are possible when the cyclic, tetrameric, or polymeric derivatives react with *n*-butyllithium. For example, nucleophilic displacement of trifluoroethoxide groups from phosphorus could occur. Alternatively, proton abstraction from a trifluoroethoxy group could be followed by coupling to another molecule or elimination of trifluoroacetaldehyde. The latter product could then presumably react further with *n*-butyllithium. Skeletal cleavage could also take place.

Mass spectral analysis of the reaction products derived from the interaction of $[NP(OCH_2CF_3)_2]_4$ with *n*-butyllithium revealed the presence of peaks from $N_4P_4(OCH_2CF_3)_7(C_4H_9)$, together with fragments from ring-coupled products. The detailed reaction pathways involved are not clear.

The reasons for the striking differences between the reactions of the cyclic trimers, **3**, **4**, or **5** and $[NP(OCH_2CF_3)_2]_4$ or n can probably be traced to two sources. First, the cyclic tetrameric, and linear polymeric skeletal structures are inherently more flexible than that of the cyclic trimer. Hence, nucleophilic displacement or skeletal cleavage reactions may proceed with greater ease. Second, the phenoxy shielding groups in **4** and **5** appear to tip the balance between reactions involving the $-OCH_2CF_3$ groups and attack on the skeleton. Cyclic, tetrameric, or polymeric analogues of **4** or **5** would most likely exhibit borderline reactivities. Even so, the discrepancy between the reactions of **3** and those of the tetramer and polymer indicate that skeletal flexibility plays a key role.

The reactions of phosphazene cyclic trimers have proved to be indispensible models for the development of synthetic routes to a wide range of phosphazene high polymers.[15] However, it is now becoming clear that this principle has limits. Cyclic tetramers may be the preferred models in circumstances where attack on the skeleton is a facile process.

Experimental

Materials. A mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ was kindly provided by Ethyl Corp. The compounds were separated and purified by fractional sublimation followed by recrystallization from hexane. Trifluoroethanol was used as received from Halocarbon Products. Sodium spheres were obtained from MCB Corp. The n-butyllithium (Aldrich) was a 1.6M solution in hexane. The electrophiles used were commercial products obtained from Aldrich or Alfa Ventron. Tetrahydrofuran (THF) (Fisher) was distilled from a potassium-benzophenone ketyl drying agent before use. THF-d8 was obtained from Aldrich. Phenol (Baker) was sublimed before use. All manipulations were carried out under a dry nitrogen atmosphere.

Analytical Techniques. NMR spectra were obtained with the use of a JEOL PS-100 FT NMR spectrometer in the FT mode, equipped with a variable temperature device. Electron impact mass spectral results were obtained with the use of an AEI MS 902 mass spectrometer. Chemical ionization mass spectral data were obtained for compounds with molecular weights below 800, with the use of a Finnegan 3200 instrument.

Synthesis of **1**, **2**, and **3**. $N_3P_3Cl_5(OCH_2CF_3)$; trans-non-gem-$[NPCl(OCH_2CF_3)]_3$ and $[NP(OCH_2CF_3)_2]_3$ were prepared from the reaction of $(NPCl_2)_3$ with sodium trifluoroethoxide in THF, as reported previously.[4] The structures were confirmed by a comparison of the ^{31}P NMR[9] values with those reported: **1** - AB_2, $\delta_A = 16.9$ ppm, $\delta_B = 22.9$ ppm ($J_{AB} = 65$ Hz); **2** - lim. AB_2, $\delta = 22.1$ ppm; **3** - A_3, 16.8 ppm. Mass spectral data: **1** - m/e calcd: 409, found :409; **2**- calcd: 537, found: 537; **3** - calcd: 728.9651, found: 728.9606.

Preparation of 4. $N_3P_3Cl_5(OCH_2CF_3)$, 1, (2.0 g, 4.86 mmol) was distilled under reduce pressure into a 3-necked flask (250 mL) fitted with an addition funnel, condenser, nitrogen inlet, and a magnetic stirrer bar. Freshly distilled THF (150 mL) was added, followed by sodium phenoxide (29.2 mmol, prepared from 2.7 g phenol and 0.67 g sodium spheres) in THF (75 mL). This mixture was boiled at reflux for 24 h and was then cooled to room temperature. The solvent was removed by rotary evaporation, and the residue was dissolved in diethyl ether. The ethereal solution was extracted with H_2O/K_2CO_3 to remove water-soluble impurities. After evaporation of the ether, the crude product was dissolved in methylene chloride and was filtered down a neutral alumina column. Removal of the solvent from the eluate yielded a colorless oil, 4, (2.5 g, 76% theor.). Mass spectrum. m/e calcd: 699.1065, found: 699.1053.

Preparation of 5. $[NPCl(OCH_2CF_3)]_3$, 2, (2.0 g, 3.71 mmol) was distilled under reduced pressure into a flask in the manner described for the preparation of 4. Sodium phenoxide (22.3 mmol, prepared from 2.1 g phenol and 0.51 g sodium spheres) in THF (75 mL) was added and the mixture was boiled at reflux for 24 h. After isolation (as above) and recrystallization from hexane, a white crystalline product was obtained, 5, (2.4 g, 91% theor.). M.p. = 55°C; mass spectrum, m/e calcd: 711.0499, found: 711.0435.

^{19}F NMR Probe Reactions. The ^{19}F NMR- monitored reactions were carried out in the following manner: 4, 5, or 3 (10 mg each) was dissolved in THF-d8 (0.75 mL) in a 5 mm NMR tube which was closed with a serum cap. This solution was cooled to -78°C in the ^{19}F NMR probe. Aliquots of *n*-butyllithium (1.6 M in hexane) were introduced via syringe and the contents were mixed quickly by inverting the tube. A ^{19}F NMR spectrum was recorded after each addition. When complete conversion to 6, 14, or 19 had taken place, an

electrophile was added as a solution in THF. (In the reactions of 19 with CH_3I or Ph_3SnCl, a more dilute mixture was used to avoid insolubility problems). Spectra were then obtained on the substituted products. The NMR tube was removed from the probe, and the contents were allowed to warm to room temperature and were concentrated on a vacuum line. Mass spectral analysis confirmed the identity of the products.

Preparation of 7, 8, 9, or 10. The following procedure is representative. Compound 4 (0.5 g, 0.72 mmol) was dissolved in freshly distilled THF (100 mL) in a flask fitted with a serum cap and a nitrogen inlet. The flask was cooled to -78°C with a dry ice/acetone bath. *n*-Butyllithium (1.14 mL of a 1.6 M solution in hexane, 1.8 mmol) was added dropwise to the stirred solution via syringe. An excess of 2-propanol (0.5 mL) was then added, and the solution was allowed to warm to room temperature. The solvent was removed by rotary evaporation, and the residue was redissolved in chloroform. The chloroform solution was filtered through a neutral alumina column, and the solvent was then removed from the filtrate under vacuum. Compound 7 (0.41 g, 89% theor.) was isolated as a colorless oil. Mass spectrum, m/e calcd: 679.1002, found: 679.0992.

Compounds 8, 9, and 10 were prepared similarly. In the case of compound 10, the final product was separated from Ph_3SnCl or $Ph_3Sn(n\text{-}Bu)$ by chromatography on silica gel using hexane eluent followed by elution with increasing amounts of chloroform relative to hexane. Mass spectral data: 8 - m/e calcd: 680, found: 680; 9 - calcd: 693, found: 693; 10 - calcd: 1028, found: 1028.

Preparation of 15-18. The procedure for the synthesis of the tri-olefinic phosphazene compounds is essentially the same as indicated above for the mono-olefinic derivatives. These species were prepared in highest yield by monitoring the addition of *n*-butyllithium to the starting material, 5, by means of ^{19}F NMR spectroscopy. When complete conversion to the lithiated intermediate, 14, was achieved, the reaction mixture was quenched with the electrophile. Alternatively, a large excess of *n*-butyllithium (3-fold) can be used and the reaction mixture is stirred at -78°C for 5 min to ensure complete conversion. The products were isolated as described above for the mono-olefinic compounds. Typical yields were in the range 55-70% theor. Mass spectral data: 15 - m/e calcd: 651.0312, found: 651.0323; 16 - calcd: 654, found: 654; 17 - calcd: 693, found: 693. (No mass spectrum was obtained for 18 due to the high molecular weight).

Preparation of 20-22. The procedure used for the synthesis of the hexa-olefinic phosphazenes was similar to that used for the tri-olefinic compounds. An excess of *n*-butyllithium (4-5 fold) was required to fully deprotonate 3 under the same conditions. Products 20-22 were isolated as described above; however, lower yields were obtained (35-50% theor.). The vinylic side groups in 20-22 are more reactive in these compounds, and some product decomposition occurs during the isolation procedure. Mass spectral data: 20 - m/e calcd: 609, found: 609; 21 - calcd: 615, found: 615; 22 - calcd: 693, found: 693.

Preparation of $[NP(OCH_2CF_3)_2]_4$ (23) and $[NP(OCH_2CF_3)_2]_n$ (24). These compounds were prepared by allowing the corresponding chloro-phosphazenes to react with an excess of sodium trifluoroethoxide, as described in previous publications.$^{1-4}$ The products were identified by comparison of the ^{31}P NMR spectra with published values: 23 - A_4, $\delta = -2.3$ ppm; 24 - $\delta = -9.8$ ppm. (The polymer spectrum was obtained in THF solvent using a D_2O-containing capillary as lock, and referenced to H_3PO_4). Mass spectrum of 23: m/e calcd: 972, found: 972.

Reactions of 23 or 24 with n-butyllithium. These reactions were carried out in the same manner as described above. The progress of each reaction was monitored by ^{19}F NMR and ^{31}P NMR spectroscopy as aliquots of *n*-butyllithium were added. In both cases, the ^{19}F peaks associated with the bound trifluoroethoxy groups (ca. 38 ppm) were replaced by a broad ^{19}F resonance at ca. 35 ppm. Similarly, the ^{31}P NMR spectra changed as follows: for 23, the singlet at -2.3 ppm was replaced by broad resonances in the range 13 to -10 ppm, and for 24, the singlet at -9.8 ppm was broadened considerably, indicating the formation of a non-discrete mixture of products.

A separate reaction was carried out in which *n*-butyllithium (0.64 mL of a 1.6 M solution in hexane, 1.03 mmol) was added dropwise to a THF (100 mL) solution of 23 (0.5 g, 0.51 mmol), which had been cooled to -78°C with a dry ice/acetone bath. After the addition was complete, a molar excess of 2-propanol was added and the mixture was allowed to warm to room temperature. Removal of the solvent on a rotary evaporator left a semi-solid material. Mass spectral analysis of the product mixture showed the following peaks of interest: m/e: 972 - 23, 930 - $N_4P_4(OCH_2CF_3)_7(CH_2CH_2CH_2CH_3)$, in addition to peaks above m/e 1600 which could correspond to fragments of coupled products.

Acknowledgment.

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References and Notes

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9. ^{31}P NMR (40MHz) spectra were for solutions in $CDCl_3$ referenced to H_3PO_4. Positive shifts represent deshielding.
10. ^{19}F NMR spectra (94 MHz) were for solutions in freshly distilled THF (with benzene-d6 lock) or in THF-d8. Fluorobenzene was used as an external reference.
11. Attempts to monitor these reactions by ^{31}P NMR spectroscopy were complicated by the similarities between the spectra of starting materials and products, and because of the complexity of the second order splitting pattern.
12. The new resonances in the ^{19}F NMR spectrum appeared as very small peaks relative to the starting material; therefore, this spectrum is not shown in Figure 1.
13. ^{13}C NMR (25 MHz) spectra were obtained with the use $CDCl_3$ solvent and

were referenced to TMS. Chemical shifts are in ppm, and coupling constants are in Hz.

14. The CH carbon atom showed different coupling constants with F_1 and F_2. The correlation between the listed J_{CF} values and the proper fluorine atoms was not ascertained.

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16. The F_1 and F_2 chemical shift assignments for **6**, **14**, **19**, **10**, and **18** are tentative.

Table I. ^{19}F NMR Data

		δ (ppm)	J_{FH} (Hz)	
1	$N_3P_3Cl_5(OCH_2CF_3)$	38.1 (t)	8	
2	$N_3P_3Cl_3(OCH_2CF_3)_3$	37.6 (m)	8	
3	$N_3P_3(OCH_2CF_3)_6$	37.5 (t)	8	
4	$N_3P_3(OPh)_5(OCH_2CF_3)$	37.8 (t)	8	Fig. 1a
5	$N_3P_3(OPh)_3(OCH_2CF_3)_3$	37.6 (m)	8	Fig. 2a

		δ - F_1[16]	δ - F_2[16]	$J_{F_1F_2}$	
6	$N_3P_3(OPh)_5(OC(Li)=CF_2)$	[23.7 (d)]	[-13.2 (d)]	104	Fig. 1c
7	$N_3P_3(OPh)_5(OCH=CF_2)$	16.4 (dd)	-3.6 (d)	66	Fig. 1e
8	$N_3P_3(OPh)_5(OCD=CF_2)$	16.2 (d)	-3.4 (d)	66	Fig. 3a
9	$N_3P_3(OPh)_5(OC(CH_3)=CF_2)$	13.5 (d)	-2.2 (d)	65	Fig. 3b
10	$N_3P_3(OPh)_5(OC(SnPh_3)=CF_2)$	[35.7 (d)]	[9.0 (d)]	44	Fig. 3c
14	$N_3P_3(OPh)_3(OC(Li)=CF_2)_3$	[23.9 (m)]	[-13.0 (m)]	104	Fig. 2b
15	$N_3P_3(OPh)_3(OCH=CF_2)_3$	16.6 (m)	-4.1 (m)	65	
16	$N_3P_3(OPh)_3(OCD=CF_2)_3$	16.3 (m)	-3.7 (m)	66	
17	$N_3P_3(OPh)_3(OC(CH_3)=CF_2)_3$	13.3 (m)	-2.3 (m))	65	Fig. 2c
18	$N_3P_3(OPh_3)(OC(SnPh_3)=CF_2)_3$	[35.6 (m)]	[8.9 (m)]	45	
19	$N_3P_3(OC(Li)=CF_2)_6$	[24.2 (m)]	[-11.6 (m)]	u	
20	$N_3P_3(OCH=CF_2)_6$	16.5 (dd)	-3.8 (d)	61	
21	$N_3P_3(OCD=CF_2)_6$	16.3 (d)	-3.5 (d)	66	
22	$N_3P_3(OC(CH_3)=CF_2)_6$	12.6 (d)	-3.7 (d)	65	

Note: u = unresolved; multiplicities do not include coupling to ring phosphorus; additional coupling constants for the following compounds were also obtained: 6: $J_{F_2P} = 5$; 7: $J_{F_1H} = 15$, $J_{F_1P} = 2$; 10: $J_{F_2P} = 9$; 15 and 20: $J_{F_1H} = 14$; 21: $J_{F_2P} = 6$.

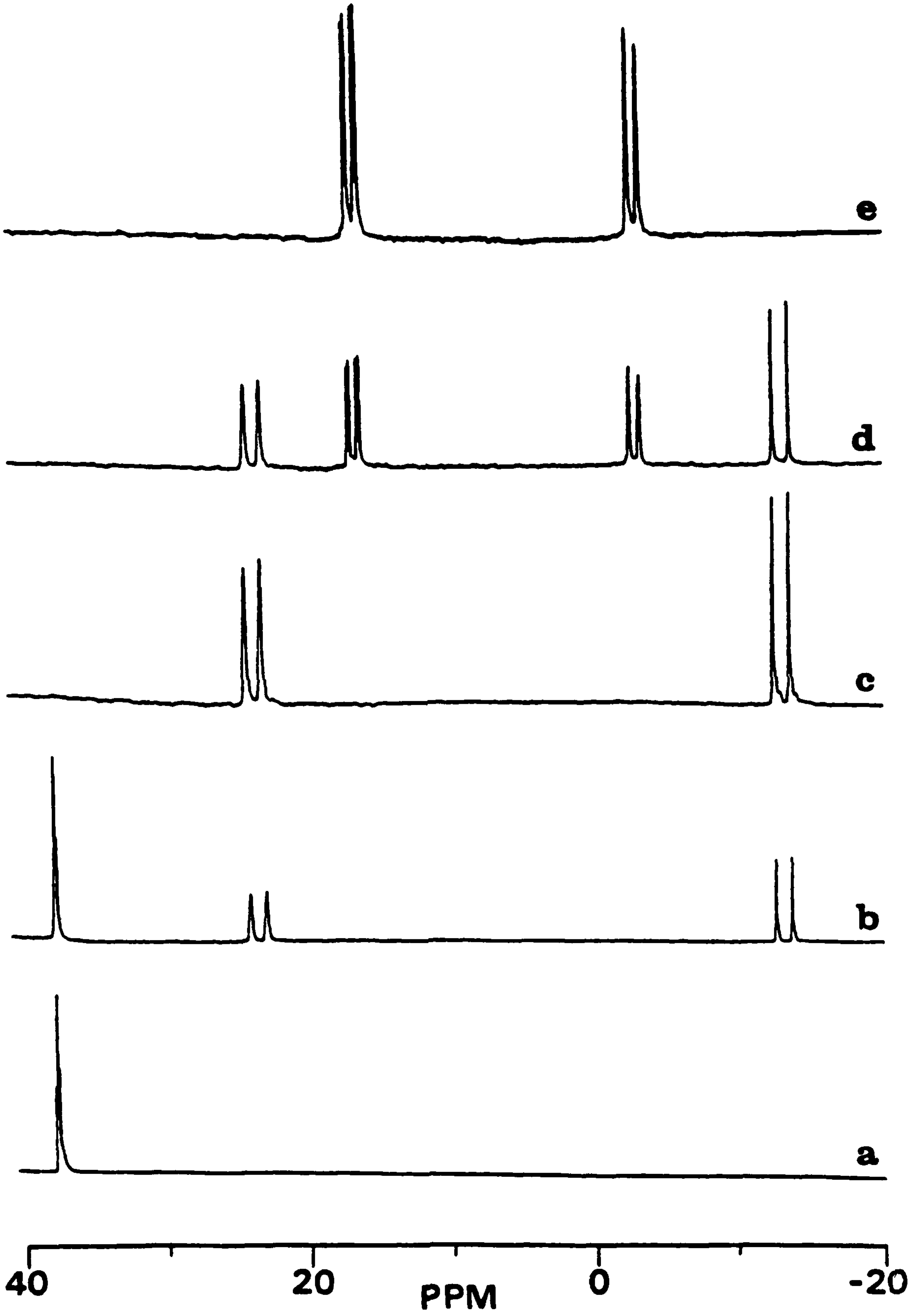
Legends to Figures

Figure 1. ^{19}F NMR spectra of (a) 4; (b) 4 plus *n*-BuLi; (c) 6 formed after reaction of 4 with 2 equiv. *n*-BuLi; (d) 6 plus 2-propanol; (e) 7 formed after reaction of 6 with 1 equiv. 2-propanol.

Figure 2. ^{19}F NMR spectra of (a) 5; (b) 14 formed after reaction of 5 with 6 equiv. *n*-BuLi; (c) 17 formed after reaction of 14 with 3 equiv. methyl iodide.

Figure 3. ^{19}F NMR spectra of (a) 8; (b) 9; (c) 10.

Figure 4 ^{13}C NMR spectra of (a) 15, proton decoupled; (b) 15, proton undecoupled. The triplet centered at 156.3 ppm is weak in spectrum (a) because no nuclear Overhauser enhancement exists for this carbon atom.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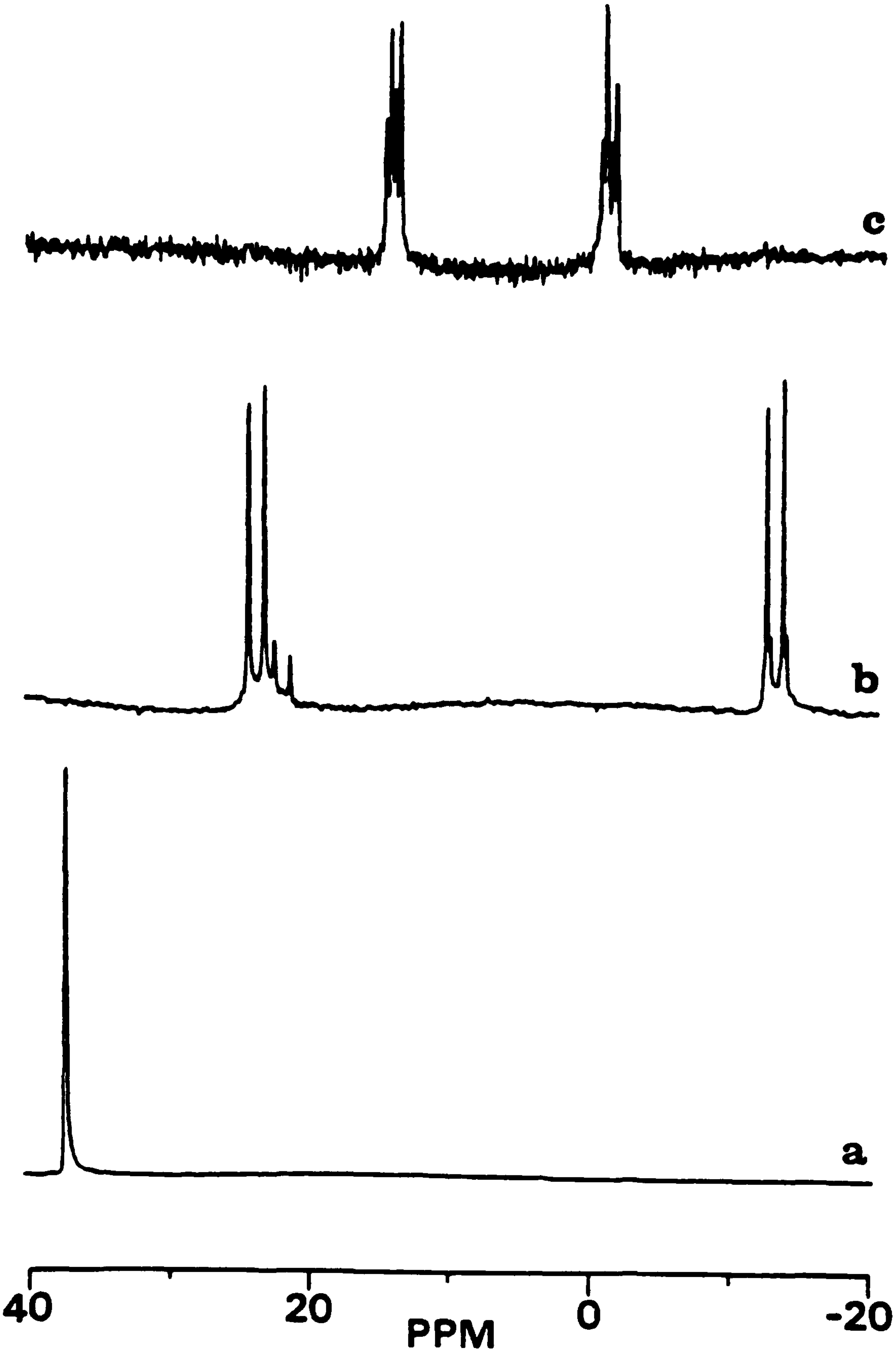
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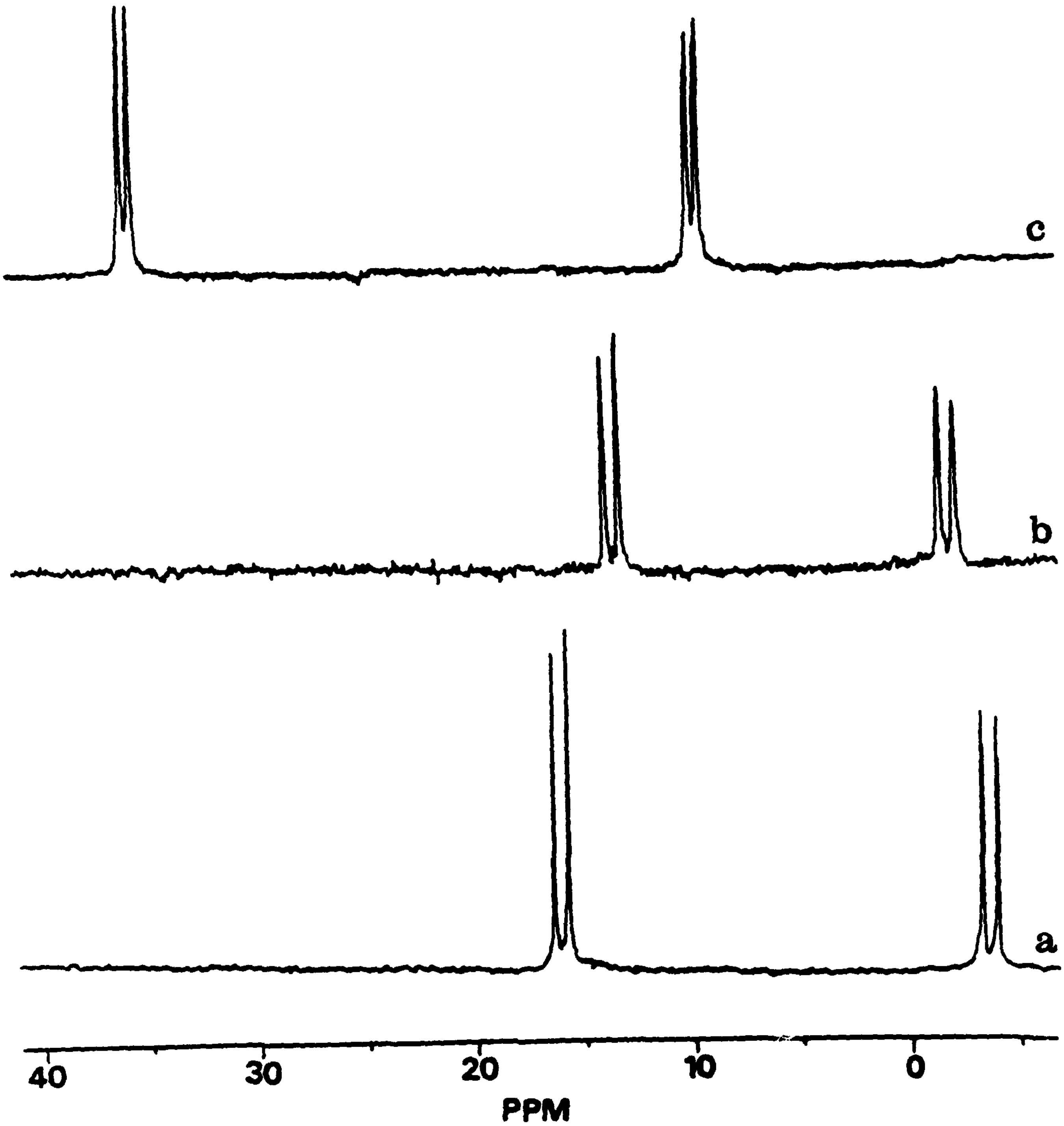
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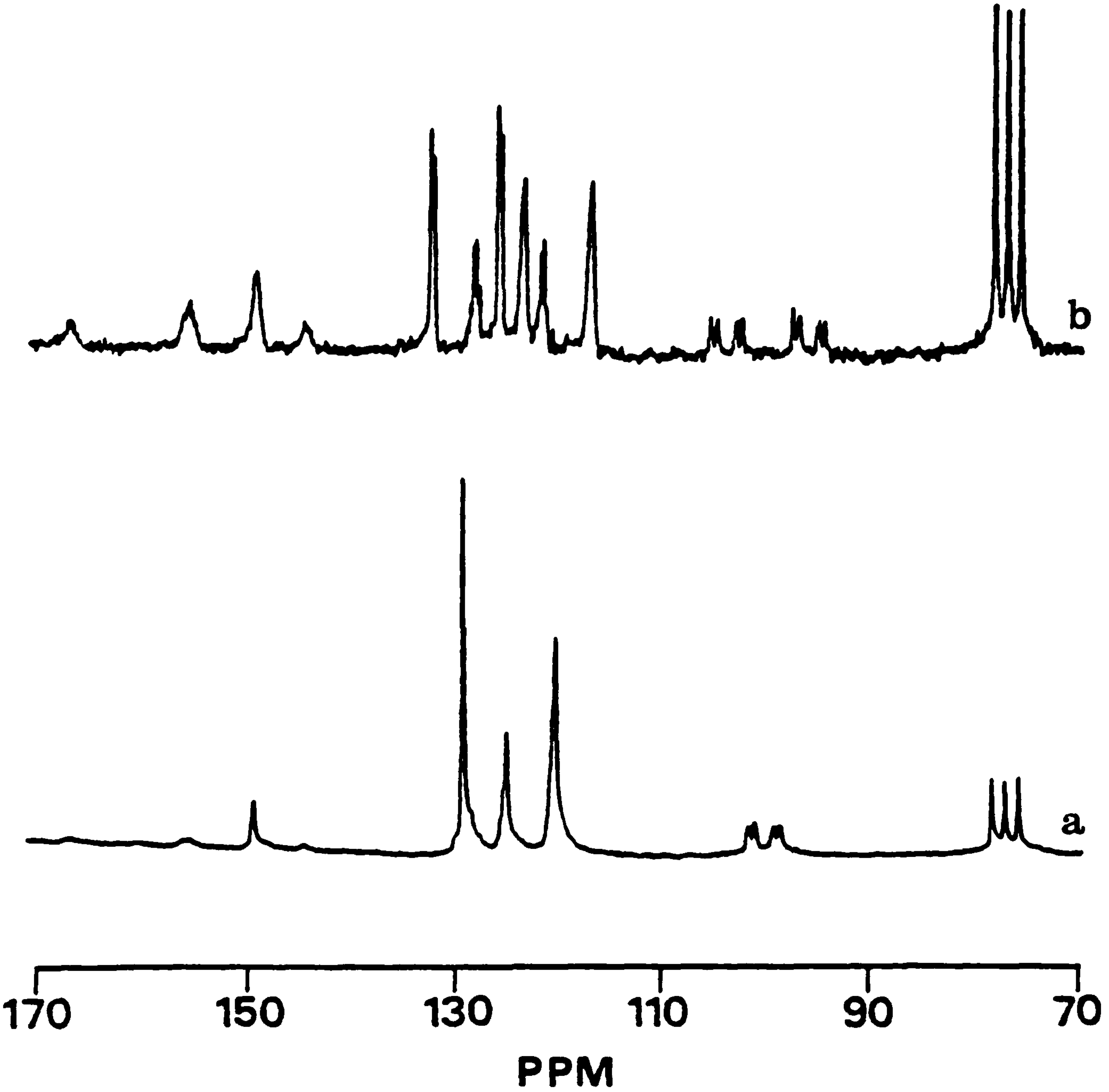
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